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by

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16. ABSTRACT The paper discusses an EPA project involving a mobile laboratory for continuous monitoring of emissions and operating parameters of hazardous waste incinerators. This Hazardous Air Pollutants Mobile Laboratory (HAPML), easily transported for use by research projects at a variety of incinerators, provides an integrated sampling and analytical package for evaluation and development of continuous and semi-continuous monitors for hazardous waste incinerators. The HAPML recently participated in a field test to examine the total mass emissions from an incinerator during steady state and transient conditions. The HAPML acquired continuous emission monitoring data and on-line gas chromatograph/flame ionization detector (GC/FID) hydrocarbon data. Volatile organic sampling train (VOST) samples were also taken. CO levels were found to be significantly higher during transient conditions and, during this particular case, to correlate with production of a product of incomplete combustion (PIC). The paper discusses the development of the HAPML, its capabilities, data obtained while monitoring a hazardous waste incinerator, and future plans.

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Wastes	Emission	Stationary Sources	14G	
Incinerators	Gas Chromatography	Hazardous Waste		07D
Mobile Equipment	Flames	Flame Ionization	15E	21B
Toxicity	Ionization		06T	07B, 07C
Sampling	Gas Ionization		14B	20I

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INTRODUCTION

The land-based incineration of hazardous waste is regulated by the Resource Conservation and Recovery Act of 1976 (RCRA I) and its 1984 reauthorization (RCRA II). Incinerators are permitted under RCRA by completing a trial burn using the types and levels of waste or an acceptable substitute to be burned in the unit and meeting certain requirements during the trial. Operating parameters established and the CO level observed during the trial burn, while the RCRA requirements were achieved, are used to determine compliance for future operation of the incinerator. The operating parameters include types of waste to be burned, feed rate, and temperature.

Although destruction and removal efficiencies (DREs) are used to indicate the performance of an incinerator, they are calculated only during the trial burn. Obtaining the information to calculate DREs is time consuming, costly, and, at the present time, not possible on a continuous basis. DREs also have a fundamental limitation: they do not take into account the presence of products of incomplete combustion (PICs). The DRE will not truly reflect the destruction and removal efficiency of a POHC if the POHC is also formed in the combustion process. Furthermore, it is possible that a different POHC can be formed in the combustion process that is more dangerous than the materials being incinerated.

Because of the interest in determining the performance of an incinerator on a real-time basis and the need to characterize the emissions from a variety of incinerators, EPA initiated a project to build a mobile laboratory for continuous monitoring of emissions and operating parameters of hazardous waste incinerators. The objective of this project was to provide an integrated sampling and analytical package for evaluation and development of continuous and semi-continuous monitors for hazardous waste incinerators. The result of the project is the Hazardous Air Pollutants Mobile Laboratory (HAPML), designed to be easily transported for use by research projects at a variety of incinerators.

This paper will discuss the development of the HAPML, its capabilities, data obtained while monitoring a hazardous waste incinerator, and future plans.

DEVELOPMENT OF THE HAZARDOUS AIR POLLUTANTS MOBILE LABORATORY

The HAPML was constructed to serve as an integrated sampling and analytical package for use in hazardous waste incineration research. The HAPML utilizes extractive sampling technology, and all components are housed in a standard 8 m long, self-propelled van.

The HAPML contains continuous monitors for real-time analysis of CO, CO_2, NO_x, O_2, SO_2, and HCl. Organic analytical instrumentation includes a gas chromatograph (GC) equipped with a flame ionization detector (FID), and a mass spectrometer (MS). All measurement sensors and the principles on which they are based are listed in Table 1. The layout inside the van is shown in Figure 1.

The sampling system delivers a portion of the gaseous effluent in the stack to the HAPML while maintaining sample integrity. Major considerations in on-line analysis include the interferences caused by particulates and moisture and minimizing reactions and interactions in the sample line.

All particulates must be removed from the sample stream because of problems they may cause in the analytical instrumentation: plugging of the lines, damage to the optical system, or light scatter resulting in erroneous data. The HAPML uses a particulate removal system located 3 m from the stack sampling port. The particulate removal system is housed in a heated aluminum filter box and consists of a high surface area, low pressure drop, spun glass-wool filter. Valves located in this box allow calibration gases to be sent from the van, through the sampling system, back to the van, and into the appropriate analytical instrument for system checks.

Water, a natural combustion product, may condense in the analyzers or can result in optical interferences. The problems may be handled in different ways depending on the species of interest. The stack gas emissions flowing to the CO, CO_2, O_2, and NO_x monitors are cooled and dried using a condenser and a Perma-Pure dryer. Since SO_2 and HCl are soluble in water, these gases would be removed along with the water. Therefore, these problems must be resolved with a different procedure. A sample conditioner is used to dilute these gas streams with dry, clean air to minimize the interference effects of water vapor. NO_2 is also soluble in water. However, since NO_x is typically about 95% NO, the loss is negligible.

Several considerations are required to ensure that reactions in the sample line do not occur. A heated Teflon line is used to transport the sample from the stack into the HAPML. The temperature of the sample line must be maintained above the boiling point of all compounds of interest. Care must be taken to eliminate any cool spots in the line, such as at

fittings. If any chlorine is in the system, stainless steel connections can react with the sample and must be removed. Teflon fittings or stainless steel fittings lined with Teflon, which eliminates contact between the stainless steel and the sample, must be used.

The organic analytical system was designed to provide information in a variety of ways. The sampling system may be used to deliver sample gas directly to the GC/MS or the GC/FID for semi-continuous monitoring, to the MS for on-line analysis of selected organic compounds, or to the FID for total hydrocarbon (THC) concentration determination. Note that the heated sample line transporting the stack effluent to the laboratory is heated to approximately 150°C. This limits the on-line organic analysis to those compounds with boiling points less than the temperature of the sample line. Many species of interest lie outside this range and may not be monitored in this fashion.

The HAPML may also be used as an on-site laboratory for analysis. It is equipped with a Volatile Organic Sampling Train (VOST) for collection and concentration of the gas effluent if the compounds of interest are present below the detection limits of the analytical instrumentation (1). These samples may be analyzed on the GC/MS or the GC/FID using a NuTech purge and trap system with a clamshell oven for thermal desorption. The purge and trap unit is equipped with a Tekmar sparger tube assembly. A quick analysis may be invaluable in determining the amount of stack gas to be concentrated to provide the proper amount of sample for more extensive analytical procedures. Also, organics collected on a sorbent material may be suspected of reacting, partially desorbing, or becoming contaminated if they are not stored properly or if they are not analyzed quickly enough. Therefore, analyzing the samples on-site improves the reliability of the results.

A two column option has recently been added to the GC to allow simultaneous operation of the GC/MS and the GC/FID. VOST samples may be analyzed on the GC/MS while the GC/FID is used for semi-continuous monitoring of selected compounds or vice versa. The only limitation is the temperature of the oven. It may be operated isothermally, or if a temperature program is used, the runs for the GC/FID and the GC/MS must be started simultaneously.

Standard gases traceable to the National Bureau of Standards (NBS) are used to calibrate the continuous emission monitors (CEMs) for quantitative analysis. Onboard storage is available for gas cylinders. A zero calibration (typically nitrogen gas) and standards in two concentrations are used each day of sampling to calibrate the instruments. The zero and the standard closer to the concentration seen while sampling are checked during the middle and at the end of the sampling period. If analyzed concentrations of these gases fall outside specified limits, the instruments are recalibrated. The values from the calibration checks are used to determine the precision and accuracy of the instruments.

The organic system is calibrated similarly, although the standards vary. When VOST analyses are being done, organic liquids are injected onto VOST cartridges, desorbed, and analyzed according to the VOST protocol. Standard gases for common organic classes are sometimes used, as well as liquids injected directly into the GC. The HAPML is also equipped with a permeation chamber for calibration of the organic system and the HCl monitor. Most analysis done with the organic system is qualitative and semi-quantitative. Precision and accuracy of the instruments are determined similarly to the CEMs.

All MS and CEM data are acquired by two onboard computers (a DEC PDP 11 and a Compaq Deskpro 286). FID data are acquired using an HP 3393A integrator. Backup of data collected is provided by strip chart recorders for the CEMs and a tape backup in the the Compaq computer.

TOTAL MASS EMISSIONS TEST

Field tests conducted by the Hazardous Waste Engineering Research Laboratory (HWERL) indicate that most facilities achieve high DREs (2). However, both the studies and the EPA's Science Advisory Board's later review raised additional questions about the performance of hazardous waste incinerators. A major concern is the unidentified emissions, both compounds referred to in Appendix VIII of the Solid Waste Methods 846 (SW846) as well as those not listed that are formed in the combustion process. The concerns expressed are not limited to simply stack emissions, but all other posssible effluents. These include organics, trace metals, and other chemicals associated with incinerator ash, spent water, and particulates. Because of this concern, HWERL initiated a project to quantify the total mass effluents (TME) from a commercial incinerator.

The TME project was conducted at a full scale, industrial rotary kiln incinerator. Two sets of triplicate 2 hour tests were scheduled. One set was performed under steady state conditions similar to those used for a trial burn. The second set of tests was conducted under transient conditions which included variations in the process similar to those expected during routine incinerator operations.

The process tested is a multiple stream hazardous waste incinerator with a horizontal rotary kiln, secondary combustion chamber, and Ceilcote ionizing wet scrubber. Waste feed streams consist of the solid waste to the kiln and a liquid mixture of organic and aqueous waste to the secondary chamber and the kiln.

During this study, three types of solid waste were fed to the kiln: alternate drums containing hydroxypropylmethyl cellulose, polyethylene wax or powder, and chlorinated pyridine tar were fed into the kiln at a rate of 20 bbl/hr (3200 l/hr). The drums began feeding into the kiln about 30 min prior to the beginning of each test period to compensate for the 30 to 60 min kiln residence time.

A single liquid organic tank was prepared with a 5% spike of carbon tetrachloride. The tank was continuously agitated to preserve homogeneity. The plant fired other wastes until the sampling crews were ready and then switched to the spiked waste. Sampling took place during this period. During the steady state tests, the liquid waste was fed into the kiln and the secondary chamber at about 2 gpm (7.6 lpm). This feed rate was increased for 7 sec approximately every 30 min to simulate the transient conditions.

As mentioned earlier, HWERL had complete responsibility for the TME test, under the direction of Robert C. Thurnau. Services of the HAPML were requested to provide CEM and on-line GC/FID data. The opportunity also allowed for further evaluation of the capabilities of the HAPML in field conditions.

HAPML TME RESULTS

CEM data were acquired every 5 sec and recorded in 30 sec averages. Table 2 lists the average concentrations for the six tests for O_2, CO_2, and CO. Tests 1 through 3 are steady state tests while 4 through 6 are transient tests. The triplicate steady state runs show very good reproducibility. The O_2 varied from 8.1 to 8.9%, the CO_2 from 6.3 to 6.4%, and the CO from 0 to 1 ppm.

Although an effort was made to achieve reproducibility for the transient tests as well, the results show a fairly wide range of values resulting from the three tests. In all cases, the peak shape for the CO concentration resulting from the induced upset and corresponding increase in CO concentration was similar. The peak maximum occurred about 1 min after the initial increase in CO concentration and did not decrease to the normal level until about 3 min after first rising above the standard concentration. The minimum level of O_2 and the maximum level of CO_2 occurred simultaneously during the transient condition. The CO_2 and O_2 appeared consistently as mirror images of the other. Typical graphs are given in Figure 2. These represent one steady state test, Test 3, and one transient test, Test 5. There is little difference between the two types of tests in the O_2 and CO_2, and the transient conditions in Test 5 are not obvious. The relationship between the time of occurrence for the extremes of the O_2 and CO_2 concentrations and the maximum in the CO concentration varied.

The GC/FID was used for on-line monitoring of low molecular weight hydrocarbons. Only methane and ethylene were detected. Table 3 gives the results. Averages of all readings for the steady state tests are given. Two averages are given for each of the transient tests. The data which occurred between the transient conditions are given under steady state, and the data acquired during the transient conditions (when CO maxima were apparent) are listed under transient. Ethylene was detected

only during the transient tests, and except in one instance, occurred simultaneously with the transient condition. Test 4 shows an obvious difference between the methane concentrations occurring between and at transient conditions. Tests 5 and 6 do not exhibit this behaviour. These data are being analyzed further.

VOST samples were taken to determine if any volatile organics were present below the detection limit of the instrument. The major peak detected could not be identified. The next two peaks in order of intensity were benzene and toluene. Benzene averaged 13 ppb for the steady state tests. Figure 3 compares the benzene concentration of the transient tests after subtracting the background or steady state level with the peak maximum of the CO concentration which occurred during the VOST run. Although data are limited, Figure 3 suggests that, while CO may not be a good indicator of DRE (3), the CO level may be related to the concentrations of at least some PICs. Each data point represents only one VOST analysis. No change was seen in the toluene concentration between the steady state and transient tests. It remained at 2 or 3 ppb for all tests.

CONCLUSIONS

The results of the field test indicate that the HAPML can be successfully operated in the field and produce quality data. Several problems in the MS have since been identified, and steps have been taken to correct them. There is, without question, a need for real-time measurement capability for hazardous waste incinerators. The HAPML provides a means of testing a number of incinerators and can be used to characterize the volatile organics and permanent gas emissions.

The present work with the HAPML is focused on determining the feasibility of using the MS as a continuous monitor. This work includes two parts. First, different chemical classes in several concentrations must be tested to ensure delivery of a representative organic sample through the sampling system to the analytical instrumentation. Once this has been successfully demonstrated, the second aspect of the work will investigate the use of the MS as a selective ion monitor (SIM) for products of incomplete combustion (PICs). One of the improvements that have been made with the MS is an upgrade in the software system to enable the SIM capabilities.

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Table 1. Measurement sensor summary.

Parameter	Instrument/Model	Measurement Principle
O_2	MSA Model 802	Paramagnetic
CO	TECO Model 48	Gas filter correlation
CO_2	MSA Model 303	NDIR
SO_2[a]	TECO Model 40	Pulsed fluorescence
NO_x	TECO Model 10	Chemiluminescence
HCl[a,b]	TECO Model 15	Gas filter correlation
Volatile Organics	Hewlett Packard 5890A	Gas chromatograph (FID detector)
	Extranuclear EL 150 (with extended range)	Mass spectrometer
Pressure	Validyne DP15-22 Differential	Pressure transducer
Temperature	Omega Type K Temperature	Thermocouple

(a) Requires the TECO 900 sample conditioner
(b) Acquired since first field test

Table 2. CEM results.

Test No.	O_2 (%)	CO_2 (%)	CO (ppm)
1	8.9	6.3	1.0
2	8.1	6.4	0.0
3	8.6	6.3	0.1
4	8.2	6.2	9.0
5	8.7	6.3	11.7
6	10.3	5.2	14.3

Table 3. Results of on-line GC/FID monitoring.

Test No.	Steady State		Transient	
	Methane (ppm)	Ethylene (ppm)	Methane (ppm)	Ethylene (ppm)
1	1.7	ND		
2	1.1	ND		
3	1.0	ND		
4	1.9	0.8	11.0	1.7
5	93.2	ND	92.9	1.3
6	48.3	ND	52.6	0.3

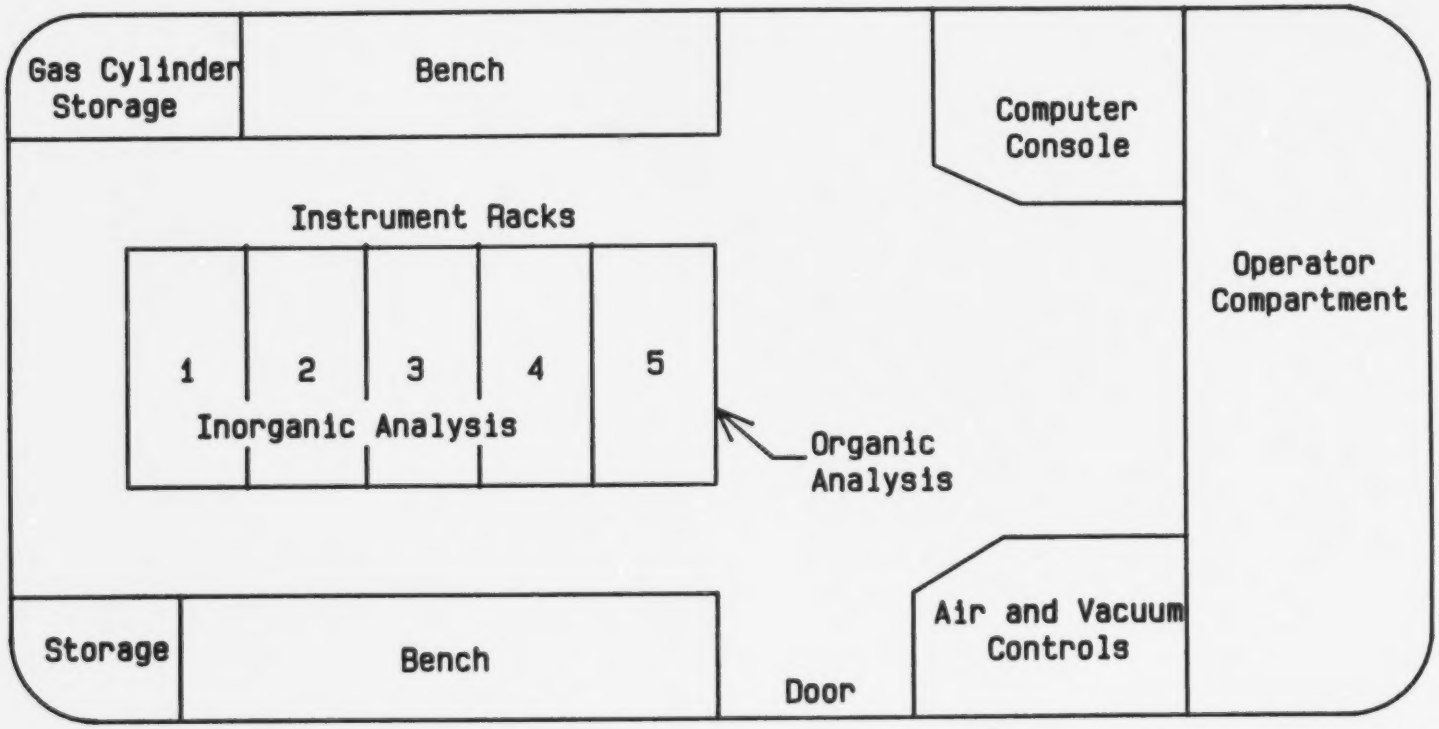

Figure 1. HAPML floor plan.

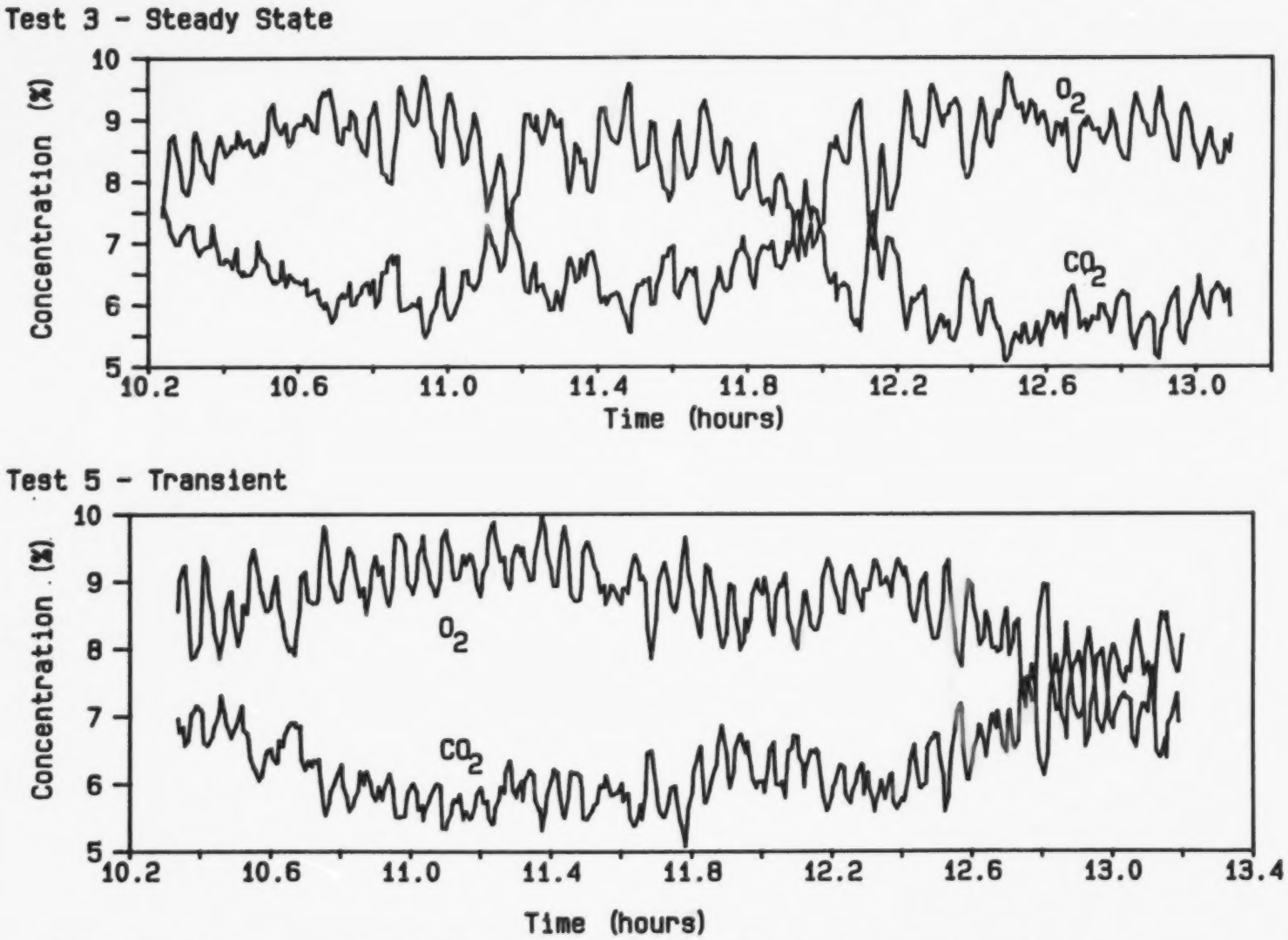

Figure 2. Comparison of CO_2 and O_2 emissions for steady state and transient conditions.

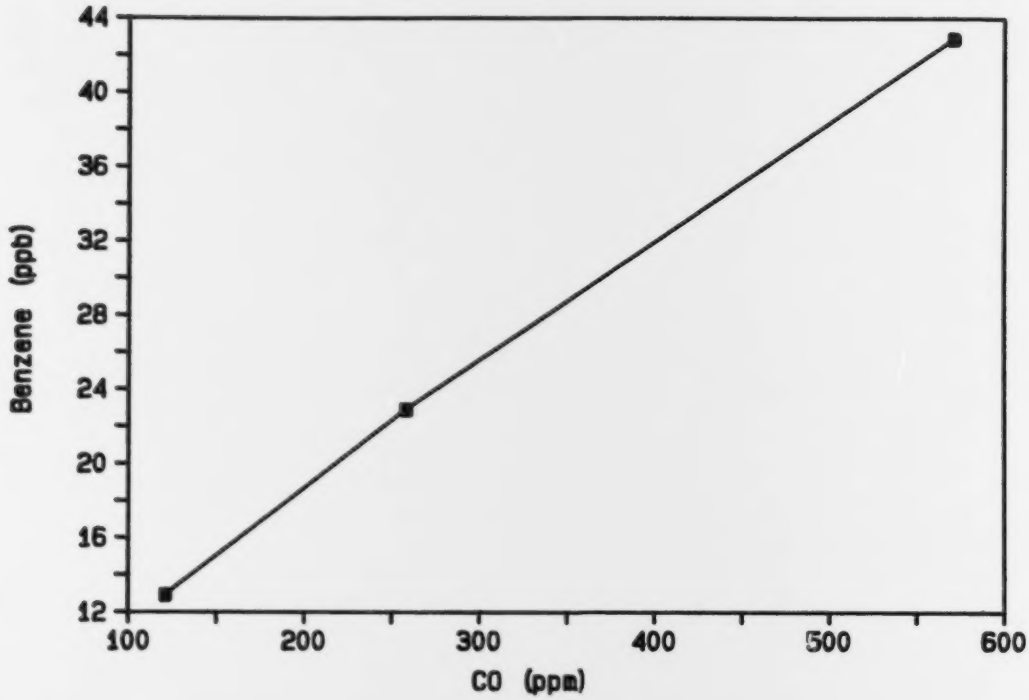

Figure 3. Comparison of benzene concentration and CO maximum concentration.